Kinetic Study of Partial Oxidation of Ethanol over VMgO Catalyst

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The gas-phase oxidation of ethanol over VMgO catalyst in the temperature range 453−513 K was studied. Characterization of the catalyst by XRD and IR spectroscopy indicated that the magnesium pyrovanadate was the active phase for oxidation. The influence of inlet ethanol concentration and oxygen partial pressure on conversion and selectivity was investigated. Acetaldehyde was formed almost selectively. CO_2 and ethylene were obtained only at the highest temperature. The catalytic function for ethanol oxidation depends on the redox ability of vanadium to alternate between different valence states. The redox mechanism was reasonable to explain the experimental results.

Introduction

The transformation of ethanol from plant raw materials, particularly in countries that do not have any natural hydrocarbon resources, is a promising process for the production of various products such as acetald hyde, ethyl acetate, acetic acid, ethylal, ETBE, etc. Acetaldehyde is a highly reactive compound and widely used as an intermediate in industrial organic synthesis. It can be produced by hydration of acetylene, vapor-phase oxidation of butane, and oxidation or dehydrogenation of ethanol (McKetta, 1988). The vapor-phase partial oxidation of ethanol over different catalytic systems has been studied by several workers (Tsuruya et al., 1985; Parlitz et al., 1985; Allakhverdova et al., 1992a,b; Bagiev et al., 1992; Quaranta et al., 1993; Castillo et al., 1993; Ling et al., 1996), and the commercial process over silver between 650 and 723 K has been performed since 1970 (Chauvel et al., 1986).

The VMgO system has proved to be efficient for the oxidative dehydrogenation of light alkanes (Chaar et al., 1987, 1988; Siew Hew Sam et al., 1990; Corma et al., 1993; Mamedov and Cortes Corberan, 1995; Carrazan et al., 1996), but as far as we know, there has been no report on its use for the oxidative dehydrogenation of ethanol. In this work, the influence of partial pressure of oxygen, inlet ethanol concentration, and temperature is investigated in the selective oxidation of ethanol over VMgO catalyst. The reaction kinetics are examined by nonlinear regression analysis.

Exp rimental Section

Catalyst Preparation. The catalyst was prepared from an aqueous solution of ammonium vanadate at 343 K, which was added to an aqueous suspension of MgO powder under stirring. The solvent was evaporated using a rotary evaporator. The solid was dried under vacuum at 343 K for 1 h, held overnight at 393 K, and calcined in air at 823 K for 8 h.

Catalyst Characterization. The specific surface area of the catalyst was determined from the nitrogen adsorption isotherm at 77 K by the BET method. A Micromeritics Accusorb 2100E and 200 mg of sample previously degassed at 513 K for 3 h wer used.

The X-ray diffraction (XRD) pattern was obtained by using a Rigaku diffractometer perated at 30 kV and 20 mA by employing Ni-filtered Cu Kα radiation (λ = 0.154 18 nm). A JCPDS-ICDD standard spectral software was used to determine the phases.

The IR spectrum was recorded by a Perkin-Elmer 683 infrared spectrometer in the region 4000−200 cm^{-1}. The sample was mixed with KBr and pressed into a thin wafer.

Catalytic Test. The catalyst (0.5−0.85 mm particle diameter) was tested in a Pyrex tubular fixed-bed reactor operated at atmospheric pressure and equipped with a jacket furnace. The reactor temperature was measured and controlled by a PID controller with a coaxial thermocouple. The feed was a mixture of ethanol, oxygen, and helium. The total flow was 50 mL/min at room temperature. The flows of oxygen and helium were controlled by Matheson mass flow controllers. Ethanol was fed from a saturator that was immersed in a water bath. Its temperature was controlled by means of a Lauda RCS-R20C cryostat, ensuring temperature variations of less than 0.1°C. The reactants and reaction products were alternately analyzed on-line by a Konic 3000 GC gas chromatograph equipped with a thermal conductivity detector. A Porapak QS (80−100 mesh) column to analyze O_2, CO_2, C_2H_4, H_2O, and oxygenated products and a 5A molecular sieve for CO, CH_4, O_2, and CO_2 were both used at isothermal conditions. The columns were arranged so that while one of them is used to analyze the gas stream the other one acts as the reference. To prevent possible condensation, all gas line connections and valves were wrapped with heating tapes. The catalytic values were obtained after running the reaction for a few hours, when the steady state was essentially reached. The conversion and selectivities to products were evaluated for the exit stream as an average of five analyses. The repeatability of the conversion data was in the range ±5%. The homogeneous contribution was tested with the empty reactor. These runs showed no activity below 553 K.

For the kinetic treatment, the weight of catalyst and the flow rate of ethanol were changed to achieve different contact times (W/F = 50−200 $g_{cat.}$ h $mol^{-1}_{ethanol}$) and different thanol conversion. Seventy-four experiments were carried out at four different temperatur s (b tween 453 and 513 K), five inlet concentrations of ethanol (3.3, 4.6, 5.7, 6.3, and 8.4 mol %), and four partial pressures of oxygen (41.3, 63.0, 94.5, and 138.6 mmHg). A set of experimental data, obtained by varying th mass velocity of the fe d, while keeping W/F constant, indicated that mass-transfer effects were negligible at the space velocities used.

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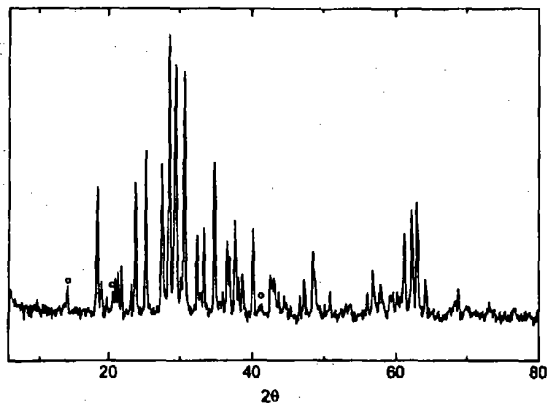

Figure 1. X-ray diagram of fresh VMgO catalyst. Peaks of α-$Mg_2V_2O_7$, ○ β-MgV_2O_6

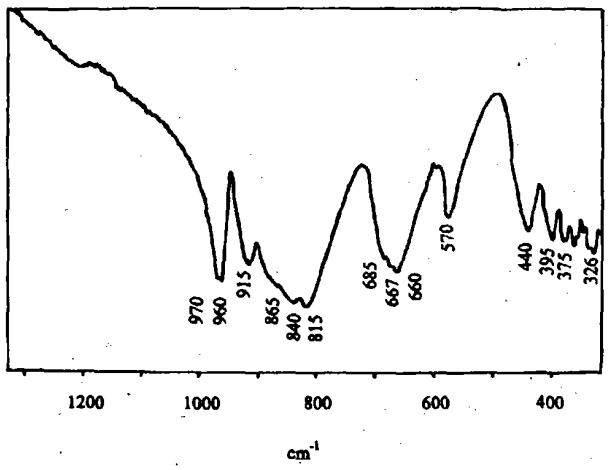

Figure 2. Infrared spectra of VMgO catalyst.

Nonlinear regression analysis was used to examine the fit of different kinetic models. For a given model, the reaction rate was integrated over the contact time, at each of the experimental conditions, to calculate the conversion predicted by the model. The Marquardt algorithm was used to search for the values of the model parameters that minimized the sum of the squared residuals.

Results and Discussion

Catalyst Characterization. VMgO catalyst was obtained from MgO and NH_4VO_3. After calcination, the catalyst was of a pale yellow color. After use, it was gray, which indicated the reduction of vanadium to an oxidation state lower than 5. The BET specific surface area was 8.8 m^2/g. Within the precision limit of the BET method no differences in surface area between fresh and used catalysts were detected. The X-ray diffraction pattern is shown in Figure 1. The spectrum revealed the dominant presence of α-$Mg_2V_2O_7$ (ASTM file 31-816) with slight impurity of β-MgV_2O_6 in good agreement with that observed by Siew Hew Sam et al. (1990). The XRD analysis of used catalyst indicated that there were no detectable differences in the bulk structure after reaction; thus, the changes to the catalyst were limited to the surface. The infrared spectrum is presented in

Table 1. Experimental Results

Y_{EtOH} (mol %)	Y_{O_2} (mol %)	W/F (g h mol^{-1})	T (K)	X (%)	Y_{EtOH} (mol %)	Y_{O_2} (mol %)	W/F (g h mol^{-1})	T (K)	X (%)
0.046	0.059	99.7	453	4.8	0.084	0.059	52.6	473	6.7
0.046	0.059	125	453	5.1	0.084	0.059	77.5	473	8.7
0.046	0.059	199.8	453	7.5[a]	0.084	0.059	105.2	473	12.9
0.046	0.059	199.8	453	7.5[a]	0.084	0.059	172.6	473	21.8
0.046	0.059	199.8	453	7.5[a]	0.084	0.059	52.6	493	15.7
0.046	0.059	99.7	473	12.3	0.084	0.059	77.5	493	20.6
0.046	0.059	125	473	13.7	0.084	0.059	105.2	493	31.6
0.046	0.059	199.8	473	21.2[a]	0.084	0.059	172.6	493	45.7
0.046	0.059	199.8	473	21[a]	0.084	0.059	52.6	513	36.3
0.046	0.059	199.8	473	20.8[a]	0.084	0.059	77.5	513	50
0.046	0.059	99.7	493	25	0.084	0.059	105.2	513	61.7
0.046	0.059	125	493	30	0.084	0.059	172.6	513	87
0.046	0.059	199.8	493	48.5[a]	0.033	0.09	199.8	453	8.1
0.046	0.059	199.8	493	46[a]	0.033	0.09	199.8	473	22.4
0.046	0.059	199.8	493	48.7[a]	0.033	0.09	199.8	493	52.8
0.046	0.059	99.7	513	55	0.033	0.09	199.8	513	88.7
0.046	0.059	125	513	65	0.046	0.09	199.8	453	8.4
0.046	0.059	199.8	513	84.6[a]	0.046	0.09	199.8	473	21.7
0.046	0.059	199.8	513	87.1[a]	0.046	0.09	199.8	493	51.6
0.046	0.059	199.8	513	85[a]	0.046	0.09	199.8	513	86.2
0.063	0.059	71.6	453	3.8	0.057	0.09	199.8	453	8.3
0.063	0.059	105.4	453	4.5	0.057	0.09	199.8	473	23.2
0.063	0.059	143.13	453	5.5	0.057	0.09	199.8	493	55
0.063	0.059	71.6	473	8.8	0.057	0.09	199.8	513	83.1
0.063	0.059	105.4	473	12.7	0.046	0.135	199.8	453	9.7
0.063	0.059	143.13	473	14.6	0.046	0.135	199.8	473	26.3
0.063	0.059	71.6	493	22.3	0.046	0.135	199.8	493	61
0.063	0.059	105.4	493	29.8	0.046	0.135	199.8	513	91.4
0.063	0.059	143.13	493	36.3	0.046	0.198	199.8	453	11.4
0.063	0.059	71.6	513	42	0.046	0.198	199.8	473	29.9
0.063	0.059	105.4	513	59.6	0.046	0.198	199.8	493	66.7
0.063	0.059	143.13	513	74.9	0.046	0.198	199.8	513	94.8
0.084	0.059	52.6	453	2.9	0.063	0.09	180.6	473	19.7
0.084	0.059	77.5	453	3.3	0.063	0.09	180.6	493	44
0.084	0.059	105.2	453	3.8	0.084	0.198	172.6	493	65.4
0.084	0.059	172.6	453	9.2	0.084	0.198	172.6	473	28.4

[a] Experimental set for diffusional control.

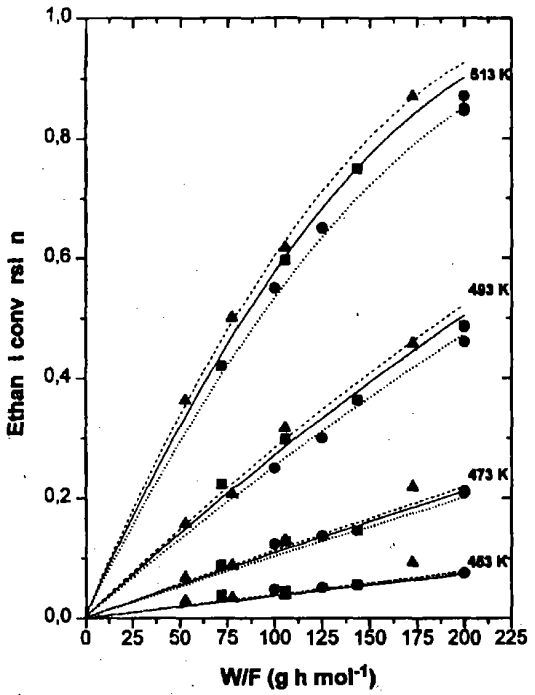

Figure 3. Ethanol conversion vs. space time at different inlet concentration of ethanol and temperatures. Curves: kinetic model, points: experimental data (partial pressure of oxygen = 41.3 mmHg). Key: ▲, 8.4 mol % of ethanol; ■, 6.3 mol %; ●, 4.6 mol %.

Table 2. Selectivity to Acetaldehyde at 513 K[a]

Y_{EtOH} (mol %)	conversion (%)	selectivity to AcH (%)
0.046	55.0	96.9
0.046	65.0	96.1
0.046	85.0	95.0
0.063	42.0	98.7
0.063	59.6	97.0
0.063	74.9	95.6
0.084	36.3	97.8
0.084	50.0	96.2
0.084	61.7	94.8
0.084	87.0	93.0

[a] Partial pressure of oxygen: 41.3 mmHg.

Figure 2. The presence of pyrovanadate was revealed through its bands (326, 362, 395, 440, 570, 667, 685, 815, 915, 960, and 970 cm^{-1}) (Siew Hew Sam et al., 1990). The bands at 970 and 960 cm^{-1} are attributed to a V=O bond characteristic of magnesium pyrovanadate. The IR spectrum confirms the X-ray diffraction.

Catalytic Results. The oxidation of ethanol over VMgO was carried out between 453 and 513 K. The experimental data are collected in Table 1. The main oxidation product was acetaldehyde with selectivity greater than 90%. At higher temperatures, CO_2, ethylene, and oxygenated products were obtained as minor products. The maximum in CO_2 selectivity was around 6%. CH_4, CO, or acetic acid was not detected under the reaction conditions used. Thus, VMgO catalyst has a high selectivity to acetaldehyde at a temperature range lower than the industrial process (McKetta, 1988; Chauvel et al., 1986). Th catalytic activity and the selectivity did not change after 12 h of reaction. No deactivation by coke formation or sintering was observed, and the catalyst can be reused without additional treatment.

Figure 3 illustrates the effect of *W/F* in ethanol conversion. These results reveal a weak influence of the inlet concentration of ethanol. As expected, the higher th temperature, the higher th conversion with only a small decrease in th selectivity, Table 2.

The depend nce f conv rsion on oxygen partial pressure was also studied in a similar manner. Figure 4 shows the conversion versus the oxygen molar fraction. The higher th oxygen partial pressure, the higher the conv rsion. In all cases, the oxygen conversion was less than 100%.

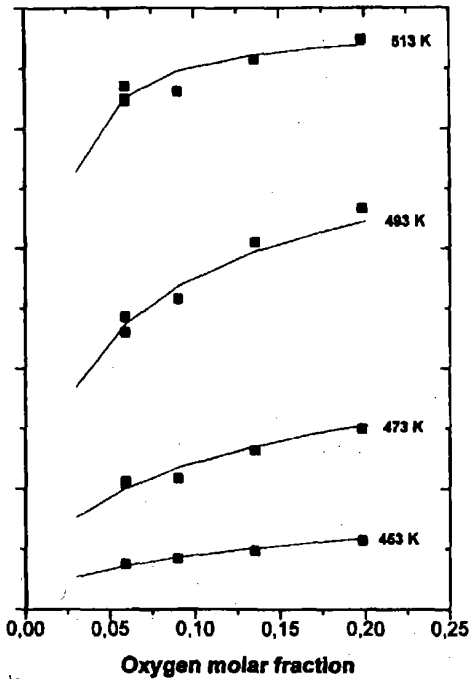

Figure 4. Ethanol conversion vs molar fraction of oxygen. Curves: kinetic model. Points: experimental data (*W/F* = 199.8 g h mol^{-1}, inlet concentration of ethanol = 4.6 mol %).

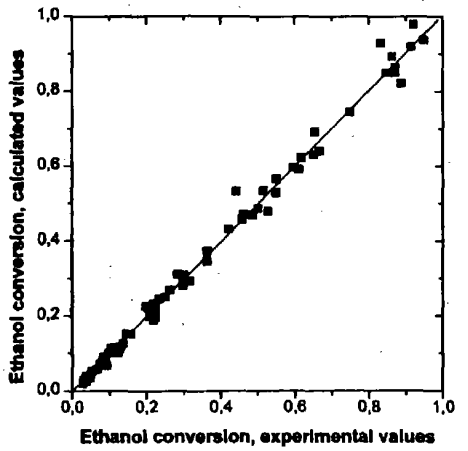

Figure 5. Parity plot for the conversion of ethanol.

Table 3. Estimation of Frequency Factors and Activation Energies from the Data at All Temperatures[a]

param	estimated value	t_{calcd}	units
k_R	k'_R: $3.34 \times 10^6 \pm 8.1 \times 10^5$	82.5	mol g^{-1} h^{-1} atm^{-1}
	E_R: 16 194 ± 385	83.3	cal/mol
k	k': $8.39 \times 10^{-3} \pm 2.2 \times 10^{-4}$	76.6	$atm^{-1/2}$
	ΔE: −7331 ± 175	83.7	cal/mol
k_O	k'_O: 3.985×10^8		mol g^{-1} h^{-1} $atm^{-1/2}$
	E_O: 23 525		cal/mol

[a] *F* value 3800. Correlation coefficient: 0.99. Confidence limits: 95%.

Table 4. Comparison with Previous Works on Different Catalysts

catalyst	activation energy (kcal/mol)	T range (K)	selectivity to acetaldehyde (%)
Cu(II)NaY (Tsuruya et al., 1985)	16.9	523–623	100
Co(II)NaY (Tsuruya et al., 1985)	15.5	523–623	100
0.5 wt % Cr/SiO_2 (Parlitz et al., 1985)	14.0	513	39.8
1.21 wt % Cr/SiO_2 (Parlitz et al., 1985)	17.5	513	66.8
V_2O_5/α-Al_2O_3 (Quaranta et al., 1993)		520	100
α-Sb_2O_4–$Fe(MoO_4)_3$ (Castillo et al., 1993)		623	92
VMgO (present work)	16.2	453–513	100–90

Reaction Kinetics. Oxydehydrogenation of ethanol to acetaldehyde and water is an exothermic reaction.

$$C_2H_5HO(g) + {}^1/_2O_2 \rightarrow CH_3CHO(g) + H_2O(g) \quad \Delta H^\circ_{298K} = -41.35 \text{ kcal/mol}$$

The VMgO system was found to be an excellent catalyst to perform this reaction at relatively low temperature. In α-$Mg_2V_2O_7$, the presence of two different bonds was found: a V=O short bond that could initiate an H abstraction and a V–O–V bond that could participate in the mechanism of water formation (Siew Hew Sam et al., 1990). During reaction, this catalyst undergoes a reduction– reoxidation cycle. A change in color from pale yellow to gray was observed after being used. A Mars–van Krevelen redox reaction mechanism (Mars and van Krevelen, 1954) can be assumed for the ethanol oxidation over VMgO catalysts. Two types of catalyst sites are considered: reduced and oxidized sites. The ethanol reacts on the oxidized site by reducing the site with a rate constant, k_R, and the reduced site is oxidized by oxygen with a rate constant, k_O. The amount of surface being covered by adsorbed intermediates is considered negligible. At steady state, the reaction rate defined as the rate of disappearance of ethanol is

$$r = k_R k_O P_E P_O^{1/2}/(k_R P_E + k_O P_O^{1/2}) = k_R P_E P_O^{1/2}/(kP_E + P_O^{1/2})$$

$k = k_R/k_O$ being a lumped parameter. This approach avoided an excessive correlation parameter. A square root dependence of the reaction rate on the oxygen partial pressure could be indicating that a dissociatively adsorbed oxygen is involved in the reoxidation step (Gellings and Bouwmeester, 1992).

The kinetic analysis of data was carried out by using the integral method. The adequacy of this model was tested by fitting the above equation to the experimental data. Parameter estimations per temperature and at all temperatures were carried out so as to obtain preexponential factors and activation energies. Figure 5 illustrates the parity plot of the overall ethanol conversion after estimation based on all temperatures. Table 3 shows the parameter estimates. The high F value and t values indicate the adequacy of the model and the significance of its parameters, respectively. From k_R and k, the activation energy and the frequency factor for the reoxidation were calculated, and they are also shown in Table 2. The activation energy of reaction, E_R = 16.2 kcal/mol, is lower than that for reoxidation, E_o = 23.5 kcal/mol, in agreement with literature (Creaser and Andersson, 1996). This indicates that th catalyst tends to be more oxidized at higher temperature, which corresponds to the higher oxidized sit concentration. The activation energy for the reoxidation reaction is near the valu found for reoxidation of vanadium in V_2O_5 catalyst (Mars and van Kr velen, 1954).

With the parameter values, the conversion was calculated by means a numerical integration of the rate equation using a fourth-order Runge Kutta method. The fitting shown in Figures 3 and 4 is satisfactory.

In Table 4, a comparison with previous works on different catalytic systems is shown. VMgO catalyst has a similar activity with a high selectivity to acetaldehyde at lower temperature.

Conclusions

From the results described above, VMgO was found to be a very active and selective oxidative dehydrogenation catalyst for ethanol. The selectivity to acetaldehyde was 100% up to 493 K, which is a temperature much lower than the one used in the industrial process. X-ray diffraction and infrared spectroscopy suggested that the active phase was magnesium pyrovanadate. The catalytic function for ethanol oxidation depends on the redox ability of vanadium to alternate between different valence states. A rate equation was developed on the basis of a steady-state redox model, and activation energies for the two partial steps were determined, which showed that the overall rate is most influenced by catalyst reoxidation. The Mars–van Krevelen mechanism was reasonable to explain the experimental results.

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